A STUDY OF THE ROLE OF ALKALI METAL SALTS AS CHAR GASIFICATION CATALYSTS BY KNUDSEN CELL MASS SPECTROMETRY

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INTRODUCTION

Although there is much current interest (1, 2)in the high-temperature reaction of oxidizing gases with carbons admixed with alkali metal salts, there is no consensus on the chemical mechanisms that comprise the process. There is general agreement that the carbon and the salt chemically interact at modest temperatures to form a catalytically active state or reactive intermediate for the oxidation reaction. The nature of this state or intermediate, however, is disputable. To search for the identity of this intermediate and to elucidate its role in catalyzing the gasification or oxidation of carbon, we have employed Knudsen cell mass spectrometry to examine the gaseous species in equilibrium with carbon-alkali metal salt admixtures at elevated temperatures.

EXPERIMENTAL

Knudsen cell mass spectrometry is a technique which reveals the gaseous species in equilibrium with a solid or liquid phase, alone or in the presence of added gases. The material of interest is loaded into the Knudsen cell, a small cylindrical container made of refractory material, with an orifice that is a very small fraction of the cell's total surface area. The cell is situated in a high vacuum system so that the orifice is in line-of-sight with a mass spectrometer ion source. An electrical resistance heating element permits the cell to be heated to high temperatures. Gaseous species formed in the cell, or introduced through an inlet tube, collide, on the average, thousands of times with the contents of the cell before they escape through the orifice. Consequently, these species can be considered to be in chemical and thermal equilibrium with the solid/liquid phases in the cell when they emerge from the orifice and are detected by the mass spectrometer. A shutter, which can be moved over the orifice, permits the cell effusate to be distinguished from the ambient gases in the vacuum system. The general experimental technique and our apparatus have been described in the literature (3, 4). In our experiments we used 100 mg samples of pure alkali metal salts or of salts admixed with Illinois No. 6 coal char or Spheron-6 channel black in Knudsen effusion cells fabricated from platinum and from graphite. We determined the relative partial pressures of vapor components by measuring their ion intensities with ionizing energies 3 to 3.5 eV greater than their respective appearance potentials, to avoid contributions to the ion signals by alternative fragmentation processes in the mass spectrometer. The absolute vapor pressure of each species was calculated by the equation,

$$P = k(I^+)(T)/\sigma$$

$$1)$$

where T is the Temperature in Kelvins, σ is the relative ionization cross-section, and k is an instrumental constant.

The particular systems of interest in this study were K_2CO_3 mixed with Spheron-6 or char, Cs_2CO_3 mixed with Spheron-6, and KBr mixed with Spheron-6. The effects of added H_2O, CO_2, CO on vapor species abundances above the K_2CO_3 admixtures were investigated in separate runs. The relative abundances of the vapor species above the pure alkali metal salts in platinum cells, were also determined.

RESULTS

Equilibrium Gaseous Species

Pure Salts

On the basis of the observed ions and their relative intensities (Table 1), we conclude that the major vapor species over $K_2CO_3(s)$ are $K_2CO_3(g)$, $K(g)$, $CO_2(g)$, and $O_2(g)$. The neutral $K_2O(g)$ appears only at high temperature in negligible amount. The vaporization processes of K_2CO_3, in the observed temperature range can be written as follows:

$$K_2CO_3(s) = 2K(g) + CO_2(g) + 1/2O_2(g) \qquad\qquad 2)$$

$$K_2CO_3(s) = K_2CO_3(g) \qquad\qquad 3)$$
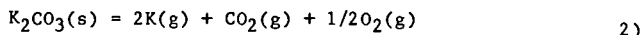
The enthalpy, ΔH, for Reaction 2 was calculated from the temperature dependence of the intensities of the gaseous ions. The value obtained, 247 (+/- 5) kJ/mol, is in agreement with the value of 251 kJ/mol calculated from JANAF data (5). The derived enthalpy of Reaction 3 was 291 kJ/mol.

The vaporization of Cs_2CO_3 was found to proceed by analogous reactions:

$$Cs_2CO_3(s) = 2Cs(g) + CO_2(g) + 1/2O_2(g) \qquad\qquad 4)$$

$$Cs_2CO_3(s) = Cs_2CO_3(g) \qquad\qquad 5)$$
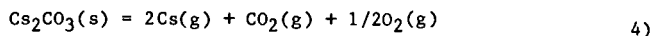
Enthalpies of vaporization were calculated from the temperature dependence of Cs^+ and $Cs_2CO_3^+$ in the temperature range 930 to 1051 K. For Reaction 4 the experimental enthalpy was ΔH = 240.3 (+/- 3) kJ/mol compared to 248.7 kJ/mol calculated from the JANAF tables (5). The enthalpy of the sublimation reaction was 251.9 (+/- 3) kJ/mol.

Carbon-Salt Admixtures

Over an admixture of K_2CO_3 and coal char (8 wt% K, mole ratio K/C = 0.029), observed in the temperature range 723 to 973 K, the only identifiable vapor species were $K(g)$, $CO(g)$, and $CO_2(g)$, suggestive of carbothermic reduction of the inorganic salt:

$$K_2CO_3(s) + C(s) = 2K(g) + CO_2(g) + CO(g) \qquad\qquad 6)$$

$$K_2CO_3(s) + 2C(s) = 2K(g) + 3CO(g) \qquad\qquad 7)$$
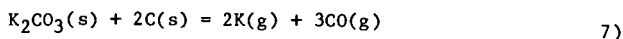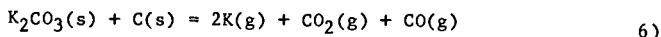
The temperature dependence of vapor pressures for $K(g)$, $CO(g)$, and $CO_2(g)$ is given in Table 2. The vapor pressures of $K(g)$ above the K_2CO_3-char sample and the pure K_2CO_3 sample are plotted in Figure 1 along with the equilibrium lines calculated from JANAF data (5) for Reactions 2, 6, and 7. The pressures of $K(g)$ above the mixture of salt with char are intermediate between those for the pure salt and for the two reduction reactions.

In a similar manner the vaporization behavior of pure Cs_2CO_3 and mixtures with Spheron-6 and coal char were investigated. A sample of Cs_2CO_3 admixed with Spheron-6 (25 wt% Cs, mole ratio Cs/C = 0.033) was studied in the temperature range 729-1059 K. The major species observed were $Cs(g)$, $CO(g)$, and $CO_2(g)$, but the CO_2^+ and the CO^+ signals decreased continuously with time (Table 3). $CsOH(g)$ was also observable in the vapor at very low partial pressures. The temperature dependence of partial pressures of the observed species above the mixture is given in the order in which data were taken in Table 3. Successive points at the same temperature demonstrate the time behavior of the signals for each species. The material removed from the Knudsen cell at the conclusion of this experiment was pyrophoric.

To provide a clue to the composition of the solid that remained in the cell, another sample of the Cs_2CO_3-Spheron-6 mixture was heated in a separate vacuum system at 800 K overnight. A portion of this vacuum-heated mixture was transfered into a capillary tube under an argon atmosphere and analyzed by X-ray diffraction. A crystalline diffraction pattern was observed but could not be identified.

In separate experiments, the equilibrium pressure of Cs above pure Cs_2CO_3, 8 wt% Cs_2CO_3 in char, 25 wt% Cs_2CO_3 in char, and 25% Cs_2CO_3 in Spheron-6 was observed. The results of these experiments are plotted in Figure 2, along with the calculated values for vaporization of the pure solid and for a possible carbothermic reduction reaction. The pressure of Cs above the Spheron-6 samples is observed to be approximately one order of magnitude higher than that above the pure salt, while the Cs pressure over the 8 wt% mixture with char is two orders of magnitude lower than that of the pure salt. Increasing the weight loading of Cs in the sample to 25% is accompanied by an increase of the Cs vapor pressure by an order of magnitude. X-ray diffraction analysis of the residual solid removed from the Knudsen cell revealed the presence of cesium aluminum silicate, $CsAlSiO_4$, among other unidentified lines.

In marked contrast to the results for the carbonate-carbon systems, samples of pure KBr and KBr admixed with Spheron-6 (4 wt%K; mole ratio K/C = 0.014) behaved identically with respect to the vaporization of K-containing species; KBr sublimation was the only observable reaction involving potassium in both samples.

Effect of Added Gases

The effects of added H_2O, CO , and CO_2 upon vapor pressure of $K(g)$ above a Spheron-6 admixture with K_2CO_3 was investigated in the graphite Knudsen cell. Effects on the K^+ signal level were studied in the temperature range 900-1100 K. During addition of the reactant gas the total pressure in the mass spectrometer was increased by a factor of 10 to approximately 1×10^{-4} Pa . Substitution of $Ar(g)$ for the reactive gases had no effect on the K^+ signal, indicating that there was no dynamic flow effect on the performance of the Knudsen cell. Addition of $CO(g)$ caused an immediate, completely reversible K^+ signal depression by 10-20%. This behavior would be expected by the effect of the law of mass action on Reactions 6 and 7. $CO_2(g)$ addition resulted in immediate depression of the K^+ level by 10% followed by a slower decrease as flow continued. When CO_2 input was discontinued, only partial recovery of the K^+ signal level occurred. A similar pattern in K^+ signal depression was observed upon addition of $H_2O(g)$. A blank run, with pure K_2CO_3 in the graphite cell at 1000 K, exhibited measurable pressures of $K(g)$ and $CO(g)$, indicative of some interaction between K_2CO_3 and the cell. However, the addition of H_2O or CO_2 had no effect on levels of CO^+ and H_2^+. The K^+ signal level was depressed by about 15% during H_2O flow, but returned to the same level after the flow was terminated. The depression of K^+ during H_2O flow is accounted for in part by the appearance of KOH^+ in the effusate at about 1% of the intensity of K^+.

As mentioned above, KBr(g) was the only K-containing vapor species detected over an admixture of KBr and Spheron-6. The addition of H_2O to the Knudsen cell gradually depressed the pressure of KBr(g); over a period of 1800 s the KBr[+] signal dropped to 50% of its initial value. At T = 945 K in the presence of H_2O, a K^{+} peak, associated with K(g) by its appearance potential, appeared in the mass spectrum and began to grow steadily. Termination of the H_2O supply caused this peak to decrease.

DISCUSSION

Comparison of the equilibrium pressures of K(g) and Cs(g) over the respective carbonates with those observed over admixtures of the carbonates and Spheron-6 or char, indicates that there is a strong chemical interaction between the salts and the carbon at elevated temperature. This interaction is not simply carbothermic reduction of the salt, as evidenced by the disparity between the calculated and the measured vapor pressures of K(g) (Figures 1 and 2). It seems likely that, in the observed temperature range, a discrete chemical compound is formed with a thermodynamic activity of the alkali metal greater than that of the carbonate but substantially below that of the pure element. The Knudsen cell data give no direct clue to the structure of this solid or liquid phase, but they do suggest that oxygen is a component because oxygen-containing gaseous species (CO and CO_2) are observed to be in equilibrium with the substance. The suppression of the pressure of molecular KBr(g) coupled with the appearance of K(g) over a KBr-Spheron admixture upon the addition of H_2O, is further evidence of an essential role of oxygen in the formation of the compound. The clear X-ray diffraction pattern obtained from the Cs_2CO_3-Spheron sample that had been heated under vacuum is indicative of a crystalline material. This pattern could not be associated with a specific chemical structure, but it was definitely not produced by Cs_2CO_3, CsOH, Cs_2O, nor by a Cs-graphite intercalation compound. Such structures have been suggested as intermediates in the alkali-metal catalyzed steam gasification of coal chars (2).

At high temperatures in the absence of an external source of oxygen, the alkali metal Spheron admixtures exhibit a gradual loss of oxygen as evidenced by the diminution in CO and CO_2 partial pressures (Tables 2 and 3). Accompanying this process, the alkali metal partial pressures increase slightly, indicative of an increase in activity with the change in oxygen stoichiometry. An opposite change occurs when the mixture is exposed to an oxidizing gas (steam or CO_2).

Based on these considerations, we propose that the chemical species formed by the interaction of alkali metal carbonates and carbon at high temperatures is a nonstoichiometric oxide that contains an excess of the metal as ions and also in a dissolved state. Metal-rich Cs-O compounds, with stoichiometries corresponding to Cs_4O and Cs_7O, have been characterized as crystalline solids at room ambient temperatures (6). At high temperatures they melt into liquid phases comprised of a higher oxide containing excess Cs (7). Information on the K-O system is available only for higher oxygen stoichiometries (8), but, by analogy, we would expect all alkali metal-oxygen systems to behave similarly.

The role of the alkali metal additive as a gasification catalyst is probably critically dependent on the formation and action of such an oxide phase. We suggest that during gasification the catalyst forms a liquid oxide film distributed over the surface of the char or carbon. (There is considerble evidence that catalyst melting does occur (10)). The composition of the film is determined by a dynamic balance between a reducing process at the carbon interface and an oxidizing process at the surface in contact with the gaseous reactant, H_2O or CO_2. At the catalyst/char interface, the anions in the catalyst react with the carbon to form an intermediate, such as a phenolate (11) that subsequently splits out CO. The anions are replenished by reaction between the oxidizing gas and the oxide at the gas/catalyst

interface. Net transport of oxygen from gas to carbon occurs by diffusion of the species in the molten catalyst film.

The presence of mineral constituents (typically SiO_2) in most coal chars complicates this picture by providing an alternative reaction path for the alkali metal salt additives. The interaction of these minerals with an alkali metal is illustrated strikingly in the case of the Cs_2CO_3-char admixture. The equilibrium partial pressure of Cs(g) over this sample is significantly lower than over pure Cs_2CO_3. Thus, the Cs activity in the solid phase is highly suppressed, as would be the case if it were chemically combined in a very stable compoud, such as the $CsAlSiO_4$ detected in the X-ray pattern of the residue. However, the low intensity of this pattern considered together with the variation in equilibrium Cs(g) pressure with the Cs content of the sample (Figure 2), suggests that all the Cs is not tied up as a discrete crystalline compound of fixed composition. It is more likely that the Cs is dissolved in an amorphous mineral glass, in which its activity is a function of its concentration.

ACKNOWLEDGMENT

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Table 1

APPEARANCE POTENTIALS AND RELATIVE INTENSITIES OF IONS IN MASS SPECTRUM OF K_2CO_3

Ion	AP(eV)	Temperature (K)	Neutral Precursor	I^+(AP + 3 eV) at 1153 K
K^+	4.3 ± 0.3	1121	K	1035
CO_2^+	13.7 ± 0.3	1121	CO_2	285
$C_2CO_3^+$	6.1 ± 0.3	1153	K_2CO_3	0.3
K_2O^+	7.8 ± 0.5	1068	K_2CO_3	2.0
K_2O^+	5.2 ± 0.5	1153	K_2O	0.03^a
O_2^+	11.9 ± 0.3	1153	O_2	33

[a]Measured at AP + 2 eV to eliminate the fragment contribution from K_2CO_3.

Table 2

PARTIAL PRESSURES OF GASEOUS SPECIES ABOVE K_2CO_3–CHAR ADMIXTURE AT VARIOUS TEMPERATURES

Temperature (K)	Partial Pressures (kPa x 10^4) K(g)	CO(g)	CO_2(g)
720	0.001	0.5	0.06
788	0.015	0.24	0.2
871	0.19	1.9	1.56
909	1.2	38.	15.1
952	5.17	53.1	2.43
978	9.68	-	-
875	0.63	1.5	0.22

Table 3

PARTIAL PRESSURES OF GASEOUS SPECIES ABOVE Cs_2CO_3–SPHERON-6 ADMIXTURES

Temperature (K)	Partial Pressure (kPa x 10^5) Cs(G)	CO(g)	CO_2(g)	(CsOH(g)
397	0	0	0.16	0
421	0	0	8.01	0
549	0	0	5.22	0
727	0	0	18.4	0
727	0	0	5.3	0
729	<0.001	0.25	1.56	0
826	0.002	3.14	14.5	0
857	0.002	3.00	4.42	0
886	0.005	3.92	2.13	0
886	0.014	1.73	0.36	0
935	0.065	9.35	1.43	0.001
936	0.33	3.77	0.11	0.001
936	0.31	1.80	0.09	0.001
992	1.41	7.96	0	0.003
1059	4.98	15.50	0	0.005
972	0.76	0.36	0	0.002

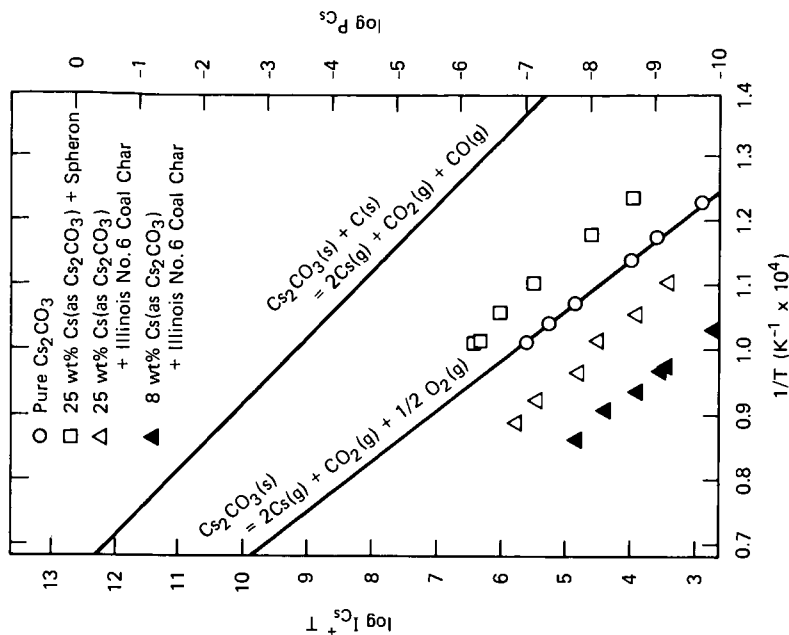FIGURE 2   COMPARISON OF CALCULATED EQUILIBRIUM Cs PRESSURES
WITH EXPERIMENTAL DATA
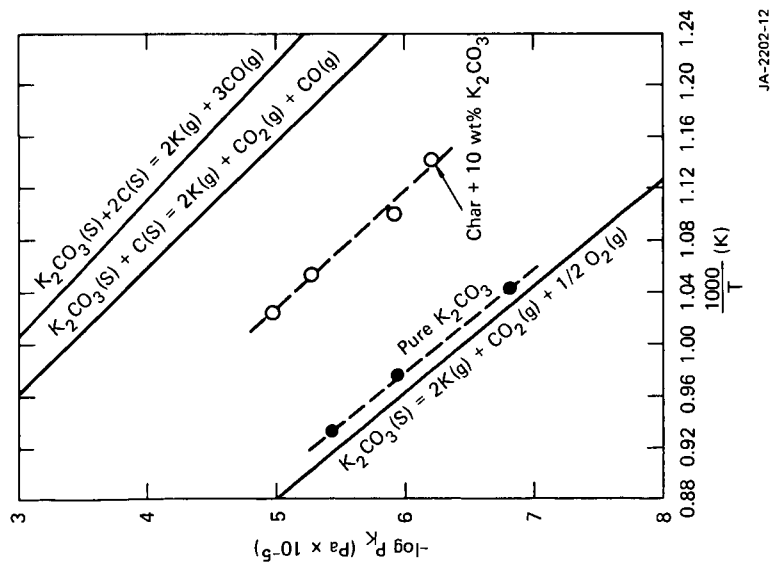
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FIGURE 1   COMPARISON OF THE CALCULATED K VAPOR PRESSURES
WITH EXPERIMENTAL DATA

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